

## LOW-MELT VISCOSITY POLYIMIDE RESINS FOR RESIN TRANSFER MOLDING (RTM) II

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### ABSTRACT

A series of polyimide resins with low-melt viscosities in the range of 10-30 poise and high glass transition temperatures ( $T_g$ 's) of 330-370 °C were developed for resin transfer molding (RTM) applications. These polyimide resins were formulated from 2,3,3',4' -biphenyltetracarboxylic dianhydride (a-BPDA) with 4-phenylethynylphthalic anhydride endcaps along with either 3,4' -oxyaniline (3,4' -ODA), 3,4' -methylenedianiline, (3,4' -MDA) or 3,3' -methylenedianiline (3,3' -MDA). These polyimides had pot lives of 30-60 minutes at 260-280 °C, enabling the successful fabrication of T650-35 carbon fiber reinforced composites via RTM process. The viscosity profiles of the polyimide resins and the mechanical properties of the polyimide carbon fiber composites will be discussed.

KEY WORDS: Polyimide, Low-melt Viscosity, High Temperature Composite, RTM370, Resin Transfer Molding, RTM, Biphenyl Dianhydride, a-BPDA

### 1. INTRODUCTION

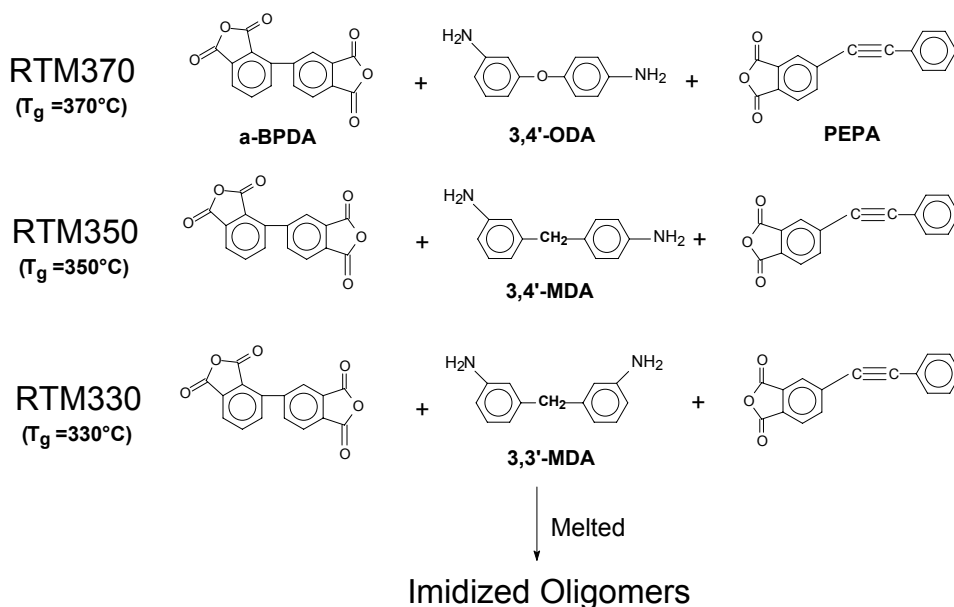
High temperature polymers have been used as lightweight composite materials for aerospace applications for decades. Polyimides, especially, play an important role for higher temperature applications beyond the capability of epoxies (177 °C) and bismaleimides, BMI, (232 °C) [1]. Most notably, PMR-15 [2] polyimide was successfully fabricated into a composite outer bypass duct for F-404 engine as a replacement for the titanium duct, leading to 30% cost savings and 12% weight savings. Under NASA's High Speed Civil Transport (HSCT) program, PETI-5 [3] was investigated extensively for airframe application during the 1980s [4]. However, both PMR-15 and PETI-5 polyimide composites require the use of prepregs or tow-pregs as well as labor intensive hand lay-up for fabrication of complicated geometries and structures. In addition, the use of organic solvents, such as methanol or N-methyl-2-pyrrolidinone (NMP), can be difficult to remove and have adverse health and safety issues during processing. In recent years, efforts have concentrated on the development of solvent-free, low-melt viscosity (10-30 poise) polyimide resins that can be adapted to low-cost resin transfer molding (RTM) or resin infusion (RI) processes.

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NASA Langley developed a series of phenylethynyl terminated imide (PETI) oligomers with low-melt viscosities (complex  $[\eta]^*$   $\sim 10$  poise as measured by rheometry) at 280 °C for resin transfer molding. PETI-298 was prepared from symmetrical 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) formulated with 1,3-bis(3-aminophenoxy)benzene (1,3,3-APB), 3,4'-oxydianiline(3,4'-ODA) and endcapped with 4-phenylethynylphthalic anhydride (PEPA) to afford a resin with  $T_g = 298$  °C [5]. However, later studies indicated that polyimides derived from asymmetrical 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) often exhibited lower melt viscosities and higher  $T_g$ 's than those prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) [6]. In pursuit of higher temperature capability and a wider processing window, PETI-330 ( $T_g = 330$  °C) was formulated using asymmetrical 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), PEPA endcap and a mixture of 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) and *m*-phenylenediamine (*m*-PDA). PETI-330 based on a-BPDA displayed better property retention at 288 °C than PETI-298 derived from s-BPDA, due to its higher  $T_g$  and corresponding softening temperature [7].

To advance to an even higher temperature capability of 315 °C (600 °F), PETI-375 [8] was developed using the same 1,3,4-APB and PEPA endcap as in PETI-330, except that 2,2'-bis(trifluoromethyl)benzidine (BTBZ) was used in place of *m*-phenylenediamine. The use of rigid BTBZ diamine raised the resin  $T_g$  to 375 °C, but it also increased the resin cost substantially, since BTBZ is expensive. PETI-298, PETI-330 and PETI-375 can all be processed by RTM to yield composites with low void content and excellent mechanical properties for applications between 260-315 °C. However, the process to synthesize these imidized oligomers required refluxing the monomers in N-methyl-2-pyrrolidinone (NMP) at  $\sim 185$  °C and removing water formed during the imidization by an azeotropic distillation using toluene. To obtain the imidized powder, the oligomer solution was poured into water and the resultant precipitate was isolated and dried in a forced air oven at 135 °C for 24 hours until it reached a constant weight to insure complete removal of high boiling NMP. Such multi-step processes to produce imidized powder are time consuming and costly.



**Figure 1** Synthesis of polyimide resins

In an effort to develop a simpler and more cost effective way to produce polyimide resins for resin transfer molding (RTM), a different approach was undertaken at NASA Glenn using a solvent-free melt process. We previously reported that a-BPDA and 4-phenylethynylphthalic anhydride (PEPA) could be mixed with either 3, 4'-oxydianiline (designated as RTM370) or 3,4'-methylenedianiline (designated as RTM350), and melted to form low viscosity resins terminated with the reactive PEPA endcap [9]. This approach uses no solvent in the process and the only volatile generated is water formed during the imidization process. In this paper, we report a new RTM imide resin based on 3,3'-methylenedianiline (designated as RTM330), and the physical and mechanical properties of its composites prepared by RTM. The corresponding data for composites produced from RTM370, RTM350 and BMI-5270-1 are provided for comparison.

## **2. EXPERIMENTAL**

### **2.1 Resin Preparation and Characterization**

A mixture of asymmetrical biphenyldianhydride (a-BPDA), 4-phenylethynylphthalic anhydride (PEPA) and the respective diamine was melted above 200 °C for 1 hour to form the corresponding phenylethynyl endcapped polyimide oligomers. The resulting solids were then ground into powders. The absolute viscosities of these imide oligomers were measured using a digital Brookfield viscometer. The rheology was performed in the parallel plate geometry with 1 g of imidized powder at a ramp rate of 4 °C/min and frequency at 10 rad/sec using an Ares Rheometer.

### **2.2 Composite Fabrication**

Composite panels were fabricated using a high temperature RTM process [10, 11]. The panels were made from T650-35, 8 harness satin weave (8HS) carbon fabrics with an 8 ply quasi-isotropic lay-up [+45/0/90/-45]<sub>s</sub>. After the tool and the injector were preheated to approximately 288 °C, 600 g of the resin was injected at 1.38 MPa and then cured at 371 °C for 2 hours. The resulting composite panels were post-cured in an oven at 343 °C (650 °F) for 8 hours to achieve the optimal mechanical properties at elevated temperature.

## **3. RESULTS AND DISCUSSION**

### **3.1 Physical properties and viscosity profiles of neat resins**

The imide resins formulated with a-BPDA, 4-phenylethynylphthalic anhydride and either 3,4'-oxydianiline (3,4'-ODA), 3,4'-methylenedianiline (3,4'-MDA) or 3,3'-methylenedianiline (3,3'-MDA), exhibited a post-cured  $T_g$ 's of 370 °C, 350 °C and 330 °C, respectively (Table 1). Therefore, they are designated as RTM370, RTM350 and RTM330 in reference to their  $T_g$ 's. The  $T_g$  of 3,4'-ODA based RTM370 is higher than that of 3,4'-MDA based RTM350. This is consistent with literature reports that indicate that polyimides containing ODA usually exhibit higher  $T_g$ 's compared to those having MDA [12]. According to the molecular simulation of

diamine monomers in polyimides, the bond angle of -O- linkage in oxydianiline is 123° while the -CH<sub>2</sub>- linkage in methylenedianiline is 111° [13]. When these short segments of oligomers are crosslinked through their reactive endcaps, the rotational barrier for RTM370 polymer chains is higher than that of RTM350's, due to the strain generated by larger bond bending within the network. On the other hand, the 3,3'-MDA based RTM330 displayed a lower T<sub>g</sub>, because of the additional kink created by the two *m*-catination as oppose to one *m*- and one *p*- linkage in 3,4'-MDA.

**Table 1 Physical Properties of Imide Oligomers/Resins Based on a-BPDA and PEPA**

Resin	Diamine	Oligomer Min. $\eta$ @280 °C by Breookfield <sup>1</sup> (Poise)	Oligomer Min. Complex $[\eta]^*$ @280°C <sup>2</sup> (Poise)	Cured Resin T <sub>g</sub> (°C) NPC <sup>3</sup> by TMA	Cured Resin T <sub>g</sub> (°C) PC <sup>4</sup> @ 650°F By TMA <sup>5</sup>
RTM370	3,4'-ODA	14	11	342	370
RTM350	3,4'-MDA	7.4	20	338	350
RTM330	3,3'-MDA	1.5	6	288	330

<sup>1</sup> Absolute viscosity measured by Brookfield Viscometer at 280 °C.

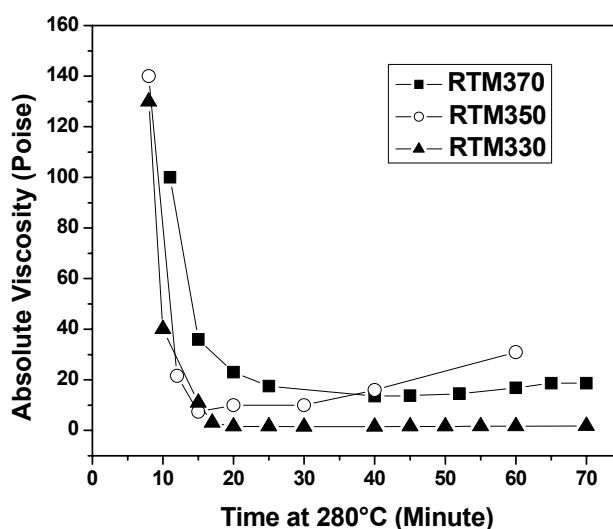
<sup>2</sup> Complex viscosity measured by Aries Rheometer, using parallel plates.

<sup>3</sup> NPC = No Post cure

<sup>4</sup> PC = Post cured at 343 °C (650 °F) for 16 hrs.

<sup>5</sup> TMA =Thermal mechanical analysis heated at 10 °C/min, using expansion mode.

Figure 2 shows that the absolute viscosity of RTM370 and RTM330, as measured with a Brookfield Viscometer at 280 °C, remain steady for 1 hour below 15 and 10 poise, respectively. However, the viscosities of RTM350 drop well below 10 poise initially, but subsequently climb up to 20-30 poise within 30-60 minutes (Fig. 2). In practice, a resin viscosity between 10-30 poises with a 1 hour pot-life (reasonable viscosity within processing window) is amenable for processing by RTM. The rheology profile of RTM370 shows a minimum complex viscosity,  $[\eta]^* = 11$  poise, and maintains a viscosity below 30 poise for 20-30 min. (Fig. 3). In contrast, RTM350 displays a minimum complex viscosity,  $[\eta]^* = 20$  poise, and has a shorter pot-life than RTM370 (Fig. 4). The complex viscosities,  $[\eta]^*$ , measured by parallel plate in a rheometer, are different from the absolute viscosities obtained from the Brookfield viscometer, because they are dependent on the experimental settings in terms of torque and tension and can vary significantly. Nevertheless, the absolute viscosities recorded by the Brookfield viscometer are more consistent and reproducible. The shorter pot-life of RTM350 arises from the presence of the methylene group (-CH<sub>2</sub>-) in 3,4'-methylenedianiline as compared to the oxygen linkage (-O-) in 3,4'-oxydianiline within RTM370. The methylene unit is believed to produce a stable benzylic free radical during cure, which can promote further crosslinking; thus, contributing to the increase in viscosity in various imide oligomers containing these units [14]. The additional crosslinking promoted by the methylene group, though not yet verified, generally yields better thermo-oxidative stability than the ether linkage in polyimides [15,16]. This trend is further confirmed by the superior thermo-oxidative stability of PMR-15 composites which contain 4,4'-methylenedianiline, relative to RP-46 based on 3,4'-oxydianiline [17].



**Figure 2 Absolute Viscosities of RTM Resins by Brookfield Viscometer at 280 °C**

**Table 2 T<sub>g</sub>'s of Polyimide/T650-35 Composites based on a-BPDA and PEPA**

Resin	Diamine	T <sub>g</sub> (°C) by DMA <sup>1</sup> NPC <sup>2</sup>	T <sub>g</sub> (°C) by DMA PC <sup>3</sup> @ 343°C (650°F)
RTM370	3,4'-ODA	324	356
RTM350	3,4'-MDA	314	337
RTM330	3,3'-MDA	334	361

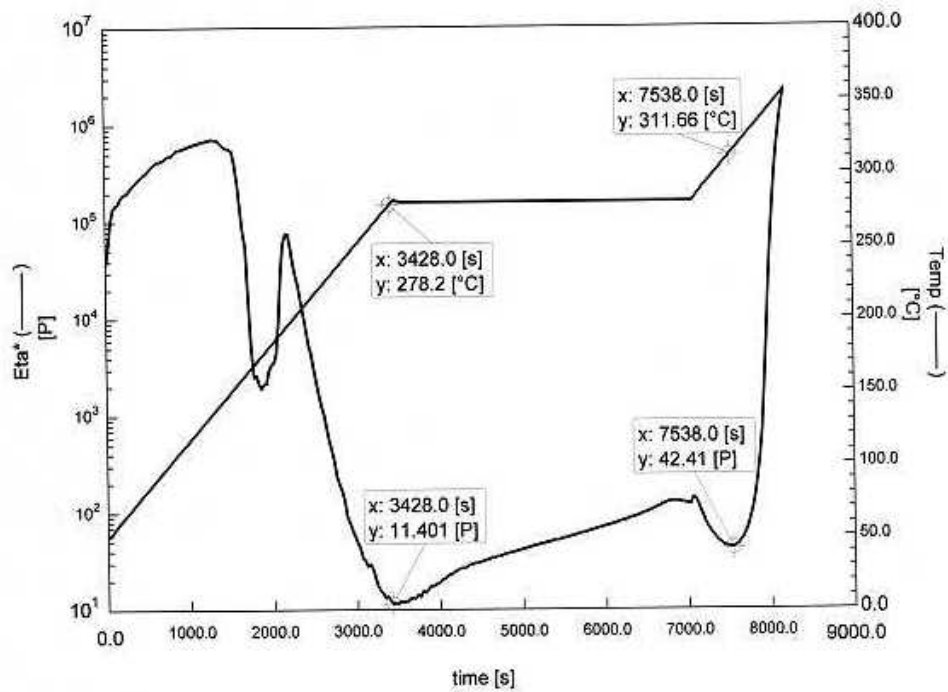
<sup>1</sup>DMA= Dynamic Mechanical Analysis were performed at 5 °C/min heating rate, using single cantilever.

<sup>2</sup>NPC = No post cure.

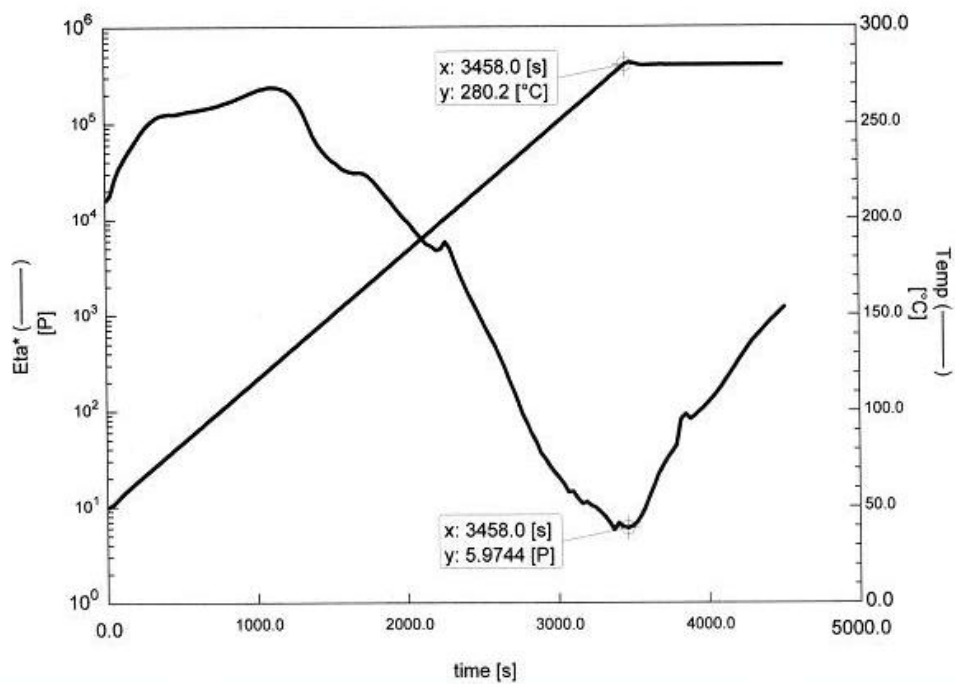
<sup>3</sup>PC = Post cured at 343 °C (650 °F) for 8 hours.

### 3.2 Characterization and mechanical properties of polyimide/T650-35 composites

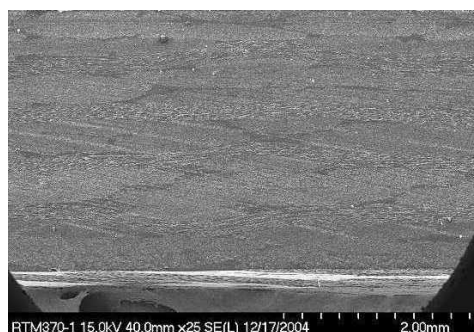
T650-35 carbon fabric reinforced composites of RTM370, RTM350 and RTM330 polyimides display T<sub>g</sub>'s of 356 °C, 337 °C and 361 °C, respectively, after post-cured at 343 °C (650 °F) for 8 hours. (Table 2). The T<sub>g</sub>'s of RTM370 and RTM350 composites are 15-20 °C lower than those of the corresponding neat resins, but surprisingly the RTM330 composite has a T<sub>g</sub> that was 30 °C higher than the corresponding neat resin's. RTM370 resin has good flow during processing because of its low viscosity and long pot-life, thus the corresponding composite exhibits very uniform resin distribution with no voids as shown in Scanning Electron Micrograph (Fig. 6a). Due to resin's higher viscosity and shorter pot-life, the resin distribution and overall quality of RTM350 composites are not very consistent throughout the panels. However, using 3,3'-methylenedianiline (3,3'-MDA) in place of 3,4'-MDA, affords a resin with better flow characteristics and pot-life, leading to composites of RTM330 (Fig. 6b) with a better quality than those fabricated from RTM350.



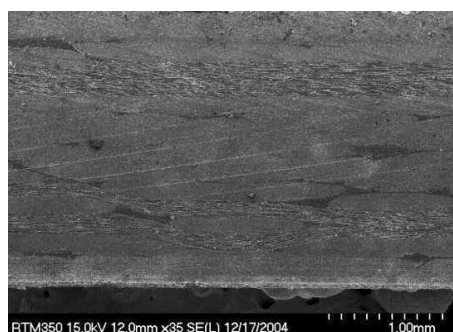
**Fig. 3 Rheology of RTM 370**



**Fig. 4 Rheology of RTM330**



**a) RTM 370**



**b) RTM330**

**Figure 6 Scanning electron micrographs (SEM) of RTM370 and RTM 350 composites**

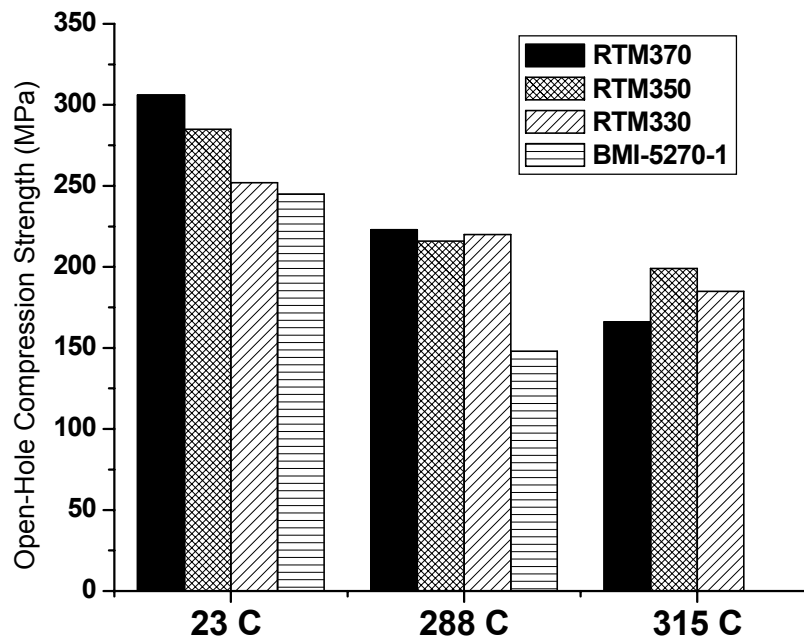
All of the polyimide composites were post cured at 343 °C for 8 hours to achieve optimal mechanical properties before testing. The mechanical properties of composites made from RTM370, RTM350 and RTM330 are compared to the state-of-the-art RTM resin, BMI-5270-1 at ambient and elevated temperatures (Table 3). RTM370 composites exhibit the highest open-hole compressive strength (Fig. 7) and modulus (Fig. 8 ) at room temperature among the three resins. However, as the test temperature is increased to 288°C (550°F), all three polyimide composites exhibit similar strength. At 315 °C, RTM350 and RTM330 composites, which contains 3,4' - and 3,3' -MDA isomers respectively, displayed better property retention than the RTM370 composite which is based on 3,4' -ODA. These phenomena are consistent with previous studies of the thermo-oxidative stability in PMR type polyimides, indicating that the ether linkage is not as stable as either methylene (-CH<sub>2</sub>-) or carbonyl (C=O) linkages [14-16]. The short beam shear strength of RTM370, RTM350 and RTM330 composites all exhibit very good property retention at 315 °C (Fig. 9).

**Table 3. Mechanical Properties of RTM370, RTM 350 and RTM330  
Compare to BMI-5270-1**

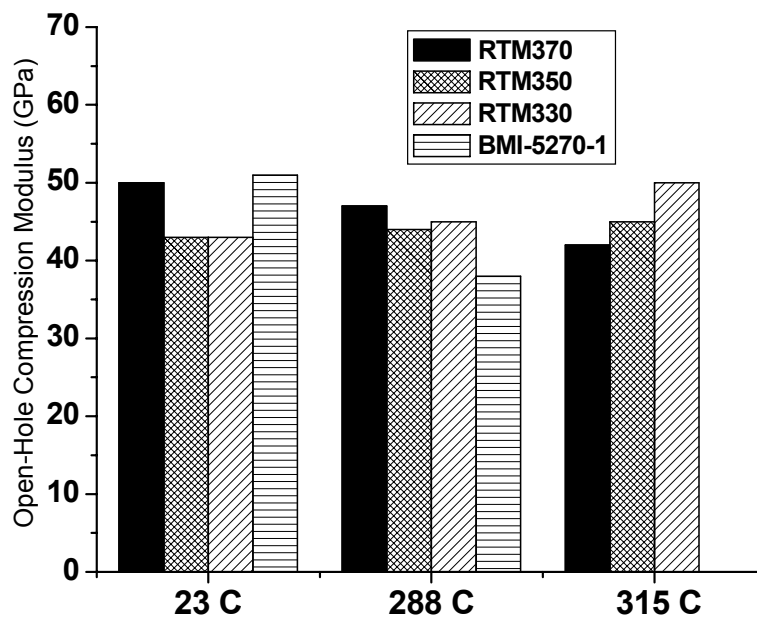
Properties	Test Temp. (°C)	RTM 370	RTM 350	RTM330	BMI-5270-1
<b>OHC Strength (MPa)</b>	23	306	285	252	245
	288	223	216	220	148
	315	166	199	185	---
<b>OHC Modulus (GPa)</b>	23	50	43	43	51
	288	47	44	45	38
	315	42	45	50	---
<b>SBS Strength (MPa)</b>	23	62	58	57	37
	288	43	32	38	14
	315	32	31	33	---

OHC = Open-Hole Compression

SBS = Short Beam Shear

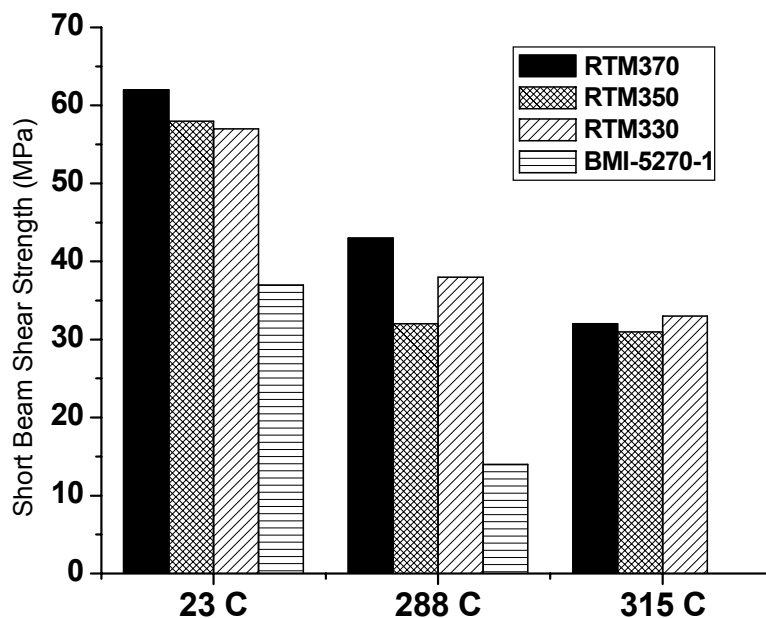


**Fig. 7 Open-Hole Compression Strength of RTM370, RTM350 and RTM330**



**Fig. 8 Open-Hole Compression Modulus of RTM370, RTM350 and RTM330**





**Fig. 9 Short Beam Shear Strength of RTM370, RTM350 and RTM330**

#### 4. CONCLUSION

A new series of imide resins (RTM370, RTM350, RTM330) based on 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) and 4-phenylethynylphthalic anhydride (PEPA) endcap, were formulated with either 3,4'-oxydianiline, 3,4'-methylenedianiline or 3,3'-methylenedianiline in a melt, without the use of a solvent. Due to the commercial availability of 3,4'-ODA, RTM370 is cheaper to manufacture than RTM 350 or RTM330. All these resins displayed low-melt viscosities in the range of 10-30 poise at 280 °C with a 1 hour pot-life as measured with a Brookfield viscometer. These resins were successfully injected into T650-35 carbon fabrics by the RTM at 288 °C (550 °F) to produce composites with low void. The elimination of organic solvents involved in the preparation of the imide oligomers by a simple melt process reduces the resin cost. In summary, RTM370, RTM350 and RTM330 all exhibited excellent open-hole compressive strength and modulus, and retained about 75% of their room temperature properties at 288 °C (550 °F). In addition, RTM370, RTM350 and RTM330 maintained 65-70% of their room temperature short beam shear strength at 288 °C. Most importantly, due to their high  $T_g$ 's, RTM370, RTM350 and RTM330 all exhibit outstanding property retention 315 °C (600 °F), exceeding state-of-the-art RTM resins, such as BMI-5270-1. These resins offer the potential of producing high temperature composites at significantly reduced cost by a) eliminating the solvent during resin synthesis and fabrication, and b) enabling the use of cost effective manufacturing methods, such as resin transfer molding (RTM) and resin infusion (RI).

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